

Ch17 Electrochemistry

①

↳ Biggest everyday overlap - listen to Radio, Start car, use calculator, anything relying on Batteries → Electrochemical Rxns are Req'd

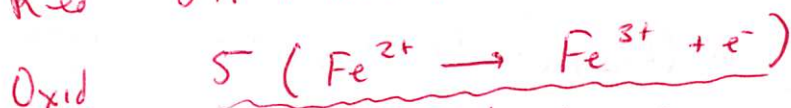
pH meters, corrosion all electrochem.

Electrochem - Study of the interchange of chemical + ~~electrical~~ electrical

17.1 Galvanic Cell

Review Back to Redox Rxns loss + gain of e⁻

(e⁻ transfer can be used to create a current.



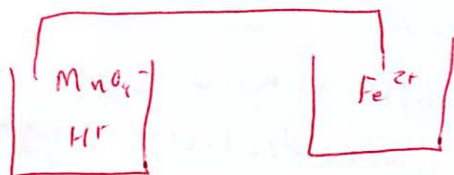
↳ This Rxn must occur 5x for the 1st to take place.

when this Rxn happens in same container NO WORK DONE

But if we sep Rxns and connect them by a wire

The transferred e⁻ can be used for useful work.

Fig 17.1



No current.

B/c left compartment would be neg + Right (A)

so charge would build up.

Keeping this charge separation Requires a large amount of E so won't happen.

a Salt Bridge or Porous disk can prevent this.

↳ They are filled w/ electrolytes which allow ion flow to balance the charge.

Now we have a Galvanic Cell - device that changes chem E to electrical E .

Fig 17.3

Cell Potential $\rightarrow (E_{\text{cell}})$ (emf) \rightarrow pull or driving force on e^-

↳ unit of Volts (V) or $\frac{J}{C}$ $\frac{\text{Joule}}{\text{coulomb}}$

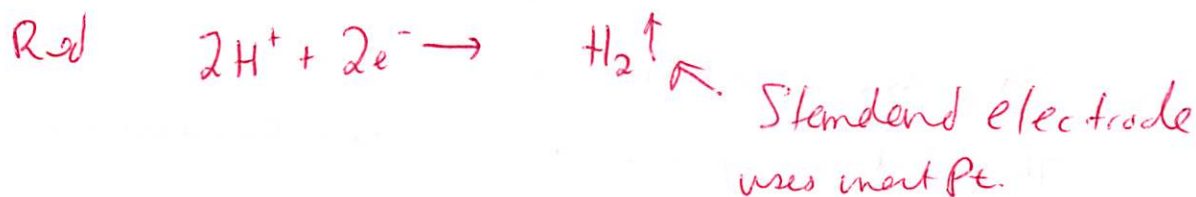
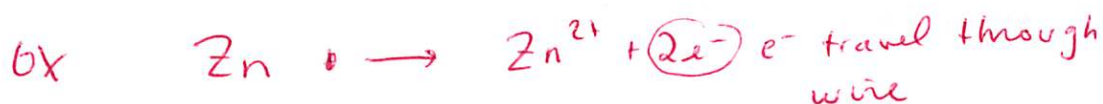
17.2 Standard Reduction Potentials

Galvanic Cells always have $2 \frac{1}{2}$ Rxns

↳ Conveniently we can find potentials of $\frac{1}{2}$ Rxns and find Potential of any Rxn.

Example.

For the Rxn @ Standard Conditions \rightarrow 1M, 1atm, 25°C



arbitrarily assigned this electrode 0.00V

So $E_{\text{H}^+ \rightarrow \text{H}_2} = 0$ for $\text{H}^+ + 2e^- \rightarrow \text{H}_2$ \leftarrow Standard Based off H_2

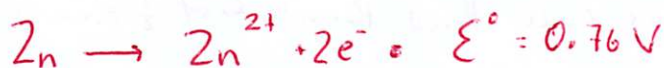
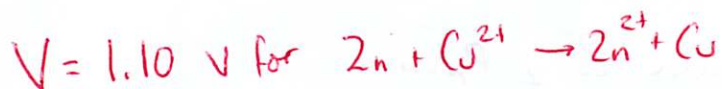
$$E_{\text{cell}}^{\circ} = E_{\text{Red}}^{\circ} + E_{\text{Ox}}^{\circ} \quad \text{Thus } \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \text{ has}$$

$$0.76\text{V} = 0\text{V} + 0.76\text{V} \quad \leftarrow \text{exa potential of } \underline{0.76\text{V}}$$

&

Now we can use this to assign Standard Potentials for anything else!

Now take Zn data and find Cu potential



$$1.10 \text{ V } \mathcal{E}_{\text{cell}} = 0.76 \text{ V} + x$$

$$x = 0.34 \text{ V}$$

Reduction

Potentials always given as Reduction

Can combine $\frac{1}{2}$ Rxns and get Bal Redox Rxn

Rules ①. A $\frac{1}{2}$ Rxn must be Reversed

The largest + potential stays as written the smaller is Reversed

$$\mathcal{E}_{\text{cell}}^\circ = \mathcal{E}_{\text{cathode}}^\circ - \mathcal{E}_{\text{anode}}^\circ$$

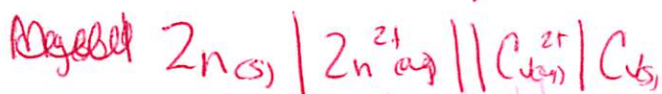
\uparrow Red \uparrow Ox

Subtraction done to Reverse the Sign.

② When $\frac{1}{2}$ Rxns are multiplied to ~~change~~ ^{bal} Eqn
Reduction Potentials are not

\mathcal{E}° is intensive prop it does not depend on ~~the~~ ^{Coefficients} Bal Rxns
That stoichiometry must be done for Rxn to occur.

Cells Written in line notation



phase defl Potm SO_4^{2-} conc here

Complete description of galvanic cell

Lab / shield #9

Includes the Rxn in cell → Cell Potential (Rxn too)

* Cell Potential

→ e^- flow direction

Setup of cell

→ Designate Anode/Cathode

what happens at each electrode

→ Nature of electrode / ions present

e^- flow?

Rxn in cell → Rxn runs spontaneously to a cell w/ a \neq potential.

Calc Cell Potential

Cell Setup → @ anode $Fe \rightarrow Fe^{2+} + 2e^-$

So need $Fe(s)$ + $1.0M Fe^{2+}$ ← anode doesn't matter
electrode

@ cathode $1M H^+, MnO_4^-, Mn^{2+}$

w/ correct conc (counter ions) to balance charge.

Pt electrode used b/c neither anion can serve as electrode



$3Fe - = 0$

17.3 Cell Potential, Electrical work, + Free E

How does thermodynamics relate to Electrochem

How much work done by cell depends on the "push" the e^- get

"Push" comes from potential difference in cell

$$\mathcal{E}_{\text{cell}} = \frac{-w}{q}$$

↖ \mathcal{E} is the work flowing out of the system
↗ q is charge

The max work a cell can do is



$w_{\text{max}} = -q \mathcal{E}_{\text{max}}$

Book talks max work.
going to ignore that

$$w = -q \mathcal{E}$$

↑ \mathcal{E} cell potential

quantity of charge

$$1 \text{ mole of } e^- = 96,485 \frac{\text{C}}{\text{mole}} = 1 \text{ F called the Faraday}$$

$$q = n \text{ F}$$

↑
mole e^-

Substitute into problem

$$w = -n \text{ F } \mathcal{E}$$

We can Relate

Free Energy & work in Section 16.9 (not covered)

$$\Delta G = w_{\max} = -qE_{\max}$$

$$\Delta G^\circ = -nFE^\circ$$

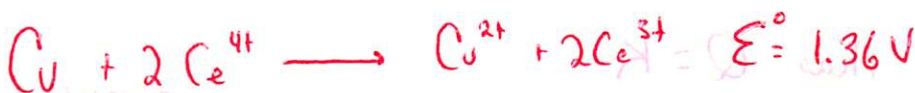
↑
Maximum cell potential is directly related to the free E

difference b/w the reactants + products in cell

This gives way to measure ΔG & and show $+E_{\text{cell}}$ is $(-)\Delta G$

17.4 Dependence of cell potential on $[E]$

So far cell are under standard (1M, 25°C, 1atm P) conditions.



what happens if $[\text{Ce}^{4+}]$ is $> 1.0\text{M}$?

Think Le Chatelier's Principle $[\text{Ce}^{4+}] \uparrow \xrightarrow[\text{Shift}]{\text{Forward}}$ in Rxn. Thus $E_{\text{cell}} \uparrow$

$[\text{Ce}^{3+}] \uparrow \xleftarrow{\text{Rev}}$ so $E_{\text{cell}} \downarrow$ b/c Rxn_{Fwd} is opposed

The Nernst Eqn

ΔG relates to $[]$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G = -nFE \quad \Delta G^\circ = -nFE^\circ$$

$$-nFE = -nFE^\circ + RT \ln Q \quad \div -nF$$

$$\boxed{E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT(\ln Q)}{nF} \text{ or } E = E^\circ - \frac{0.0591}{n} \log Q} \quad \text{at } 25^\circ\text{C}$$

Both on
AP Exam
Eqn list

Now we can calculate potential when Reactants / Products
not @ standard state.

Calculation of K via Redox

$$E_{\text{cell}} = 0 \quad \text{thus } Q = K$$

B/c FWP = Rev

using Nernst

$$E = E^\circ - \frac{0.0591}{n} \log Q$$

$$0 = E^\circ - \frac{0.0591}{n} \log K$$

$$\text{thus } \boxed{\log K = \frac{nE^\circ}{0.0591}} \quad \text{at } 25^\circ\text{C}$$

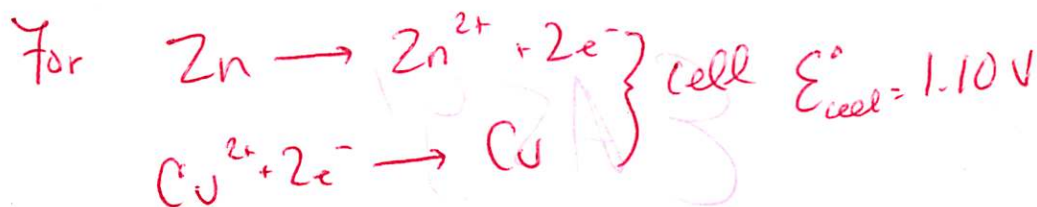
Electrolysis

5

17.7 Galvanic Cell \rightarrow Reaction Proceeds Spontaneously

Electrolysis \rightarrow E needed (elec current) to produce chemical change

\hookrightarrow def: forcing a current through a cell to produce a chemical change for which a $E_{cell}^{\circ} < 0$



I current applied that is $> 1.10 \text{ V}$ the cell will flow backwards!
get Electrolytic Cell - cathode/anode switch / ion flow switch.

Stoichiometry of Electrolysis

\hookrightarrow how much chem Δ occurs w/ the Flow of a current for specific time.

How much Cu is plated when 10.0 amps runs for 30.0 min.

$$\text{Ampere (Amp)} = \frac{1 \text{ Coulomb}}{\text{Sec}}$$

Process: $\begin{array}{c} \text{Current} \\ + \\ \text{Time} \end{array} \longrightarrow \begin{array}{c} \text{quant} \\ \text{of charge} \\ \text{Coulomb} \end{array} \longrightarrow \text{mol } e^{-} \longrightarrow \begin{array}{c} \text{mol} \\ \text{element} \end{array} \longrightarrow \begin{array}{c} \text{mass} \\ \text{element} \end{array}$

Eqn used: $I = \frac{q}{t}$ ← change (C)

↑
current
A (C/s)

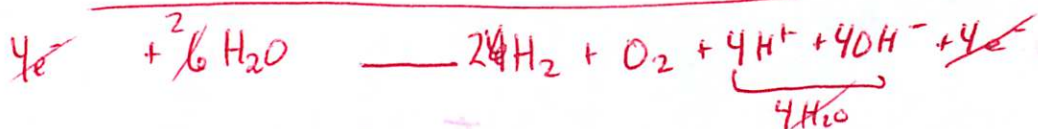
↑
t (s)

$$\left(10 \frac{C}{s}\right) (30.0 \text{ min}) \left(\frac{60s}{1 \text{ min}}\right) = 1.80 \times 10^4 C \times \frac{1 \text{ mole}^-}{96500 C} \times \frac{1 \text{ mol Cu}^0}{2 \text{ mole}^-} \times \frac{63.5 \text{ g Cu}}{1 \text{ mol Cu}} = \boxed{5.94 \text{ g Cu}}$$

Stoich

EASY!

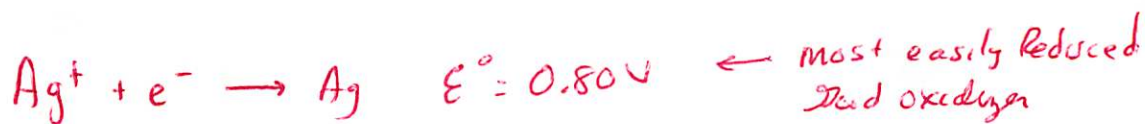
You've all seen H_2O electrolysis



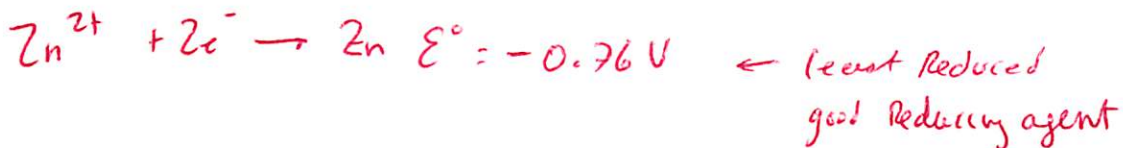
Need ions to get going

B/c in pure H_2O not enough ions to allow current to flow.

Electrolysis of Mixtures



Red oxygen



good Reducing agent

Reduction Potentials are activity series

Demo's

electrolysis of KI

pencil lead
+ 9V Battery



Not always true

in NaCl Soln $\rightarrow \text{H}_2\text{O}, \text{Na}, \text{Cl}^-$



due.

Doesn't happen b/c More V is Req'd than expected

Called 'overvoltage' \rightarrow difficulty transferring e^- from soln to atoms across electrode soln interface.

~~Compare~~ actually how NaOH made largest use of Elec
What @ Cathode
 $\text{Na}^+ + e^- \rightarrow \text{Na}$
or
 $2 \text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$